standard). The aryl proton at the 3 position of the naphthalene moiety appears as a sharp singlet at 8.88 ppm. On addition of *n*-butylamine these peak positions change smoothly to 3.20 and 9.01 ppm, respectively, at the highest concentration of *n*-butylamine. Throughout this nearly ninefold change in the amount of *n*-butylamine added to the solution, and in spite of the large upfield shift of the α-methylene protons, the relative areas of the methylene proton triplet and the H-3 singlet remained constant at 2:1. This can only be consistent with eq 6 and not with 15, since in eq 15 this ratio of areas should increase as the equilibrium is shifted to the right.

Additional evidence for eq 6 lies in the fact that the stoichiometry established for the product equilibrium, K_p is that of eq 6, and is inconsistent with eq 15. If the reaction in eq 15 were primarily to the first complex (zwitterion), no dependence of K_p on *n*-butylammonium ion should have been found, and if the reaction were to the second complex, there should have been a square dependence on *n*-butylamine concentration.

Kinetic Procedures. Rates were measured photometrically by means of either conventional or stopped-flow technique. For the conventional technique, a Cary-14 spectrophotometer equipped with a special thermostated cell holder which maintained temperature constant within ±0.02° was employed. Reaction solutions were prepared as follows: standard solutions of amine, amine hydrochloride, and tetrapropylammonium iodide in DMSO were prepared; for a given run, appropriate volumes of the appropriate solutions were combined and diluted quantitatively with DMSO at room temperature; 3.00 ml of the resulting solution was placed in a cuvette which was allowed to come to thermal equilibrium in the cell compartment; 20 μl of a standard solution of substrate was injected and mixed; and absorbance at the chosen wavelength was followed with time. For the stopped-flow technique, a Durrum–Gibson stopped-flow spectrophotometric apparatus was employed.

Acknowledgments. We are grateful to Professor C. F. Bernasconi for critical discussions and for information about experiments in progress and to Mrs. Carol Cornelson King for assistance with some of the experiments.

A Study of the Photolytic Stabilities of Fluoroalkyl Iodides by Electron Spin Resonance Trapping Techniques and the Temperature Dependence of the Nitroxide Splitting Constants

Kenneth J. Klabunde

Contribution from the Department of Chemistry, University of Iowa,
Iowa City, Iowa 52240. *Received August 22, 1969*

Abstract: Radicals formed by the photolysis of fluoroalkyl iodides have been trapped with 2-nitroso-2-methylpropane (NOMP), and the resultant esr spectra have been analyzed. Relative photolytic stabilities of the iodides were determined by competitive photolysis and trapping experiments. The results show that the groups which allow facile radical formation are in the order $C_6H_5 > Cl \gtrsim CF_3CF_2 > CF_3 > F > H$. In addition, temperature studies with several of the trapped radicals have shown large changes in fluorine splitting constants. These changes can be rationalized in terms of preferred structural conformations at low temperatures as well as fluorine–nitrogen p–π interactions.

Several esr studies of chemically trapped short-lived free radicals have recently appeared.[1-7] Diphenylnitrone,[3] phenyl-*t*-butylnitrone (PBN),[3,5,6] and 2-nitroso-2-methylpropane (NOMP)[1,2,4] have been used successfully. The latter reagent has been employed for the study of radicals formed by photolysis,[1] polymerization,[4] and γ-ray bombardment.[2] In the present work NOMP was used to study the photochemical formation of fluorinated alkyl free radicals from fluoroalkyl iodides.

Recently, interest has grown in the elucidation of the effectiveness of through space fluorine p–π interactions (*cf.* Discussion) first invoked by Sheppard. Substituent effect studies have indicated that this interaction may be quite important.[8,9] However, initial opposition to this concept has helped to instigate additional work in the area.[10] Esr studies have been useful in this respect. Fluorinated aryl radical anions have shown temperature-dependent fluorine splittings which have been rationalized in terms of p–π interactions.[11,12] Fluorine–nitrogen p–π interactions have been indicated by esr studies. Strom and Bluhm[13] rationalized unusually large fluorine splittings using this interaction concept. Sheidler and Bolton[14] have presented some of the strongest evidence for fluorine–nitrogen p–π interactions. These workers found that

---

(1) A. Macker, Th. A. J. W. Wajer, Th. J. DeBoer, and J. D. W. vanVoorst, *Tetrahedron Lett.*, 2115 (1966).

(2) C. Lagercrantz and S. Forshult, *Nature*, 218, 1247 (1968).

(3) M. Iwamura and N. Inamoto, *Bull. Chem. Soc. Jap.*, 40, 702, 703 (1967).

(4) G. R. Chalfont, M. J. Perkins, and A. Horsfield, *J. Am. Chem. Soc.*, 90, 7141 (1968).

(5) E. G. Janzen and B. J. Blackburn, *ibid.*, 90, 5909 (1968); 91, 4481 (1969).

(6) Janzen and Blackburn[5] have carefully characterized phenyl-*t*-butylnitrone (PBN) as a trapping agent. It has been pointed out, however, that PBN is not effective as a trap for large radicals such as heptafluoroisopropyl[7] and triphenylmethyl.[5] Also, PBN is slightly susceptible to photolysis itself, and in the present work it was found that the large fluoroalkyl radicals (formed from the photolysis of the corresponding iodides) were not trapped by PBN. Instead, the PBN broke down upon photolysis to yield a small amount of NOMP which trapped the fluoroalkyl radicals. Thus, nearly identical esr spectra were obtained by the photolysis of heptafluoroisopropyl iodide in the presence of PBN or in the presence of NOMP. (Diphenylnitrone was also found to decompose upon photolysis.)

(7) E. G. Janzen, private communication.

(8) W. A. Sheppard, *J. Am. Chem. Soc.*, 87, 2410 (1965).

(9) W. A. Sheppard, *Trans. N. Y. Acad. Sci.*, (2) 29, (6), 700 (1967).

(10) M. J. S. Dewar and A. P. Marchand, *J. Am. Chem. Soc.*, 88, 354 (1966).

(11) J. C. Danner and A. H. Maki, *ibid.*, 88, 4297 (1966).

(12) M. T. Jones, *J. Chem. Phys.*, 42, 4054 (1965).

(13) E. T. Strom and A. H. Bluhm, *Chem. Commun.*, 115 (1966).

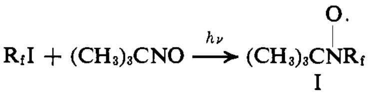
(14) P. J. Sheidler and J. Bolton, *J. Am. Chem. Soc.*, 88, 371 (1966).

A_N and A_F were temperature dependent in the esr spectrum of bistrifluoromethylnitroxide. (Sheppard and Sharts[15] have presented a recent review of this area.)

In the present study, temperature dependence of A_F and A_N have been observed in fluoroalkyl radicals trapped by NOMP. This study has helped to elucidate the relative importance of fluorine-nitrogen p–π interactions as opposed to preferred structural conformations at low temperatures.

Method and Results

The photolysis of benzene or methylene chloride solutions of NOMP and various fluoroalkyl iodides led to stable fluorinated nitroxides (I).[16] The radical I was stable at room temperature for hours and could be conveniently studied by esr. The efficiency of NOMP for trapping R_f radicals is quite good, and comparison



$$R_fI + (CH_3)_3CNO \xrightarrow{h\nu} \underset{\mathrm{I}}{(CH_3)_3C\overset{O\cdot}{\overset{|}{N}}R_f} \qquad (1)$$

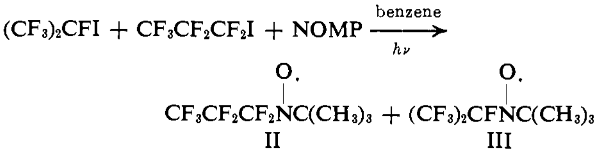
studies indicated that it is at least as efficient as PBN (which has been reported as 80% efficient in trapping thermally produced phenyl radicals).[5] In addition, although NOMP is susceptible to photolysis by red, visible, or uv light and forms *t*-butyl radicals (which are trapped by additional NOMP to form di-*t*-butylnitroxide), if even a slight excess of R_fI was present, only I could be detected by esr. Further, I is formed irreversibly, and does not exchange when $R_f'I$ is added to it. In each case the fluorine splittings (A_F) in the esr were quite large, and each R_f grouping resulted in a very distinctive esr pattern. Table I summarizes the splitting constants obtained from structures such as I.

Table I.[a] Splitting Constants (Esr) for Benzene Solutions of Photolyzed Fluorinated Iodides and NOMP[b]

Iodide[c]	A_N	$A_\beta{}^F$	$A_\gamma{}^F$	$A_\beta{}^H$
CF_3I	12.05	12.05		
CF_3CF_2I	11.10	21.85		
$CF_3CF_2CF_2I$	11.31	18.58		
$(CF_3)_2CFI$	11.92	2.25	2.25	
$(CF_3)_2CHI$	12.21		2.31	0.72
$(CF_3)_2CDI$	12.14		2.32	

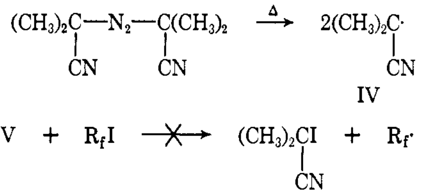
[a] Each value is an average of several determinations, and calculated from Fieldial calibrations in gauss. These values were usually reproducible to ±0.05 and always within ±0.10 G. [b] Photolysis of NOMP alone yielded di-*t*-butyl nitroxide. A_N = 15.09 G; previously reported as 15.18 G (H. LeMaire, A. Rassat, and P. Servoz-Garin, *J. Chim. Phys.*, **59**, 1247 (1962)). [c] Two other iodides were studied, but the spectra obtained were quite complex and the analysis of these spectra will be presented elsewhere. These iodides were 2-iodo-2-phenylhexafluoropropane and 2-chloro-2-iodohexafluoropropane (*cf.* Experimental Section).

Photolytic Stability Studies. During photolysis studies of various fluorinated iodides in the presence of NOMP, it was noted that some iodides yielded stronger esr signals than others. Therefore, competition experiments were initiated. Benzene solutions of NOMP and two R_fI compounds were photolyzed, and the esr spectra analyzed. Since each iodide yielded a very characteristic esr spectrum, the spectroscopic separation of two radicals trapped simultaneously could be easily made. Equation 2 may serve as a typical example. The amount of II *vs.* III formed is indicative



$$(CF_3)_2CFI + CF_3CF_2CF_2I + NOMP \xrightarrow[h\nu]{\text{benzene}} \underset{\mathrm{II}}{CF_3CF_2CF_2\overset{O\cdot}{\overset{|}{N}}C(CH_3)_3} + \underset{\mathrm{III}}{(CF_3)_2CF\overset{O\cdot}{\overset{|}{N}}C(CH_3)_3} \qquad (2)$$

of the ease of photolysis of heptafluoroisopropyl iodide *vs.* heptafluoro-*n*-propyl iodide. Figure 1 illustrates the spectrum obtained from the reaction outlined in eq 2. The outer lines are due to nitroxide II while many of the inner lines are due solely to III. By measurement of these lines quantitative determinations of the amount of II *vs.* III were possible. Table II summarizes the competition experiments studied and gives the per cent of one radical trapped *vs.* its partner. Longer periods of photolysis yielded more intense signals, but the same ratios of II/III were obtained. As has been pointed out above, I is formed irreversibly. In addition, it is unlikely that any reaction of $R_f\cdot$ with $R_f'I$ to form $R_f'\cdot$ and R_fI occurs before trapping of $R_f\cdot$ by NOMP for two reasons: (a) identical experiments with R_fI plus $R_f'I$, and with only R_fI yielded spectra of approximately the same signal intensities for the trapping of $R_f\cdot$. Therefore, the presence of $R_f'I$ did not significantly affect the amount of $R_f\cdot$ trapped. This observation indicates that the $R_f\cdot$ trapped was indeed due to photolysis of R_fI itself; (b) thermal decomposition of azobisisobutyrinitrile in the presence of R_fI and NOMP in benzene yielded no detectable amounts of I.[17] Only the nitroxide due to the trapping of IV was observed.[18] Therefore, the



$$(CH_3)_2\underset{CN}{\underset{|}{C}}{-}N_2{-}\underset{CN}{\underset{|}{C}}(CH_3)_2 \xrightarrow{\Delta} \underset{\mathrm{IV}}{2(CH_3)_2\underset{CN}{\underset{|}{C}}\cdot}$$

$$\mathrm{IV} + R_fI \not\longrightarrow (CH_3)_2\underset{CN}{\underset{|}{C}}I + R_f\cdot \qquad (3)$$

reaction sequence outlined in eq 3 is not operative and suggests that exchange between $R_f\cdot$ and $R_f'I$ is not operative either. In addition, it should be noted that the larger fluoroalkyl radicals were invariably formed in larger amounts. Therefore, the argument that smaller radicals may be more efficiently trapped by NOMP due to steric interactions is not applicable. However, another possible difficulty in these studies should be mentioned. It is possible that R_f radicals may be trapped not only by NOMP but also by R_f–NOMP adduct. The relative size of k_2 and k_3 should be dependent on steric considerations. As discussed previously, however, k_2 probably does not change

---

[15] W. A. Sheppard and C. M. Sharts, "Organic Fluorine Chemistry," W. A. Benjamin, Inc., New York, N. Y., 1969, p 38.

[16] Proof that I is indeed the correct structure for these nitroxides has been indicated by several considerations: (a) examination of a series of these compounds has yielded esr results that would be predicted by structural considerations; (b) the spectra obtained are predictable based on similar nitroxides reported;[14] (c) 2-deuterio-2-iodohexafluoropropane was synthesized and studied as an additional check on the structure of I. As expected, the proton splitting observed with the 2-hydro-2-iodohexafluoropropane disappeared when the 2-deuterio compound was substituted for it in the analysis.

[17] If light was not strictly excluded from the sample, I could be detected.

[18] A^N = 14.95 G.

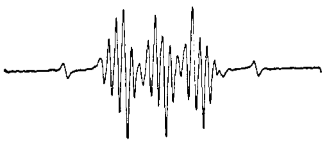
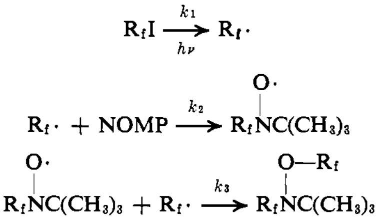


Figure 1. Esr spectrum of a mixture of II and III. The complete scan is 50 G. The complex triplet structure in the spectrum is due mainly to III. In this nitroxide all of the fluorines are magnetically equivalent at room temperature. Thus, a triplet (equal intensities for A_N) of octets is observed for III. Superimposed is the spectrum of II which is a triplet (equal intensities for A_N) of triplets where A_F is larger than A_N (*cf.* Table I). The extreme outer lines are due to II.

appreciably with change in R_f size since then it would be expected that larger R_f radicals would yield less intense esr signals than the smaller ones; this is not the case. It is more difficult to say if k_3 is large and if it varies significantly with change in R_f. However, if



$$R_fI \xrightarrow[h\nu]{k_1} R_f\cdot$$

$$R_f\cdot + \text{NOMP} \xrightarrow{k_2} R_f\overset{\text{O}\cdot}{\text{N}}\text{C}(\text{CH}_3)_3$$

$$R_f\overset{\text{O}\cdot}{\text{N}}\text{C}(\text{CH}_3)_3 + R_f\cdot \xrightarrow{k_3} R_f\overset{\text{O}-R_f}{\text{N}}\text{C}(\text{CH}_3)_3$$

the variance in k_3 were a dominant feature of the experiments, then similar sized R_f groups should yield similar esr intensities; this is also not the case as can be seen in Table II in experiments 3 and 4. The steric requirements of $(CF_3)_2CF$ and $(CF_3)_2CH$ should be about the same.

Table II. Relative Amounts of Fluoroalkyl Radicals Trapped by NOMP during Simultaneous Photolysis

Expt	Fluoroalkyl iodides	% fluoroalkyl[a] radical trapped
1	CF_3I	2.2
	$(CF_3)_2CFI$	97.8
2	CF_3CF_2I	13.8
	$(CF_3)_2CFI$	86.2
3	$CF_3CF_2CF_2I$	23.1
	$(CF_3)_2CFI$	76.9
4	$(CF_3)_2CHI$	27.6
	$CF_3CF_2CF_2I$	72.4
5	$(CF_3)_2CClI$	98.9
	$CF_3CF_2CF_2I$	1.1
6	$(CF_3)_2CIC_6H_5$	100.0
	$CF_3CF_2CF_2I$	0.0

[a] Each number is an average of at least two determinations. The reproducibility was quite good and nearly always within 2%.

Temperature Studies of Nitroxides. Quite large changes in fluorine splitting constants have been observed for some of the nitroxide radicals studied. It has been reported that low temperatures cause A_F to increase in bistrifluoromethyl nitroxide.[14] However, in the present work A_F has been found to be dependent on the nitroxide formed. Both increases and decreases in A_F have been noted with a decrease in temperature. Table III summarizes the splitting constants observed at various temperatures for nitroxides formed by photolysis of four fluoroalkyl iodides in the presence of NOMP. Figures 2 and 3 illustrate the significant spectral changes that occur as temperature is changed.

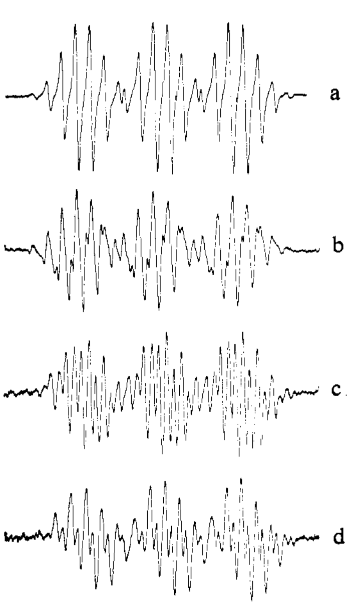


Figure 2. Esr spectra of nitroxide formed from photolysis of heptafluoroisopropyl iodide in the presence of NOMP: (a) 25°, (b) −30°, (c) −60°, (d) −90°. Each complete scan is 50 G. Spectrum (a) indicates the magnetic equivalence of all the fluorines in III at 25°. Thus, a triplet (equal intensities for A_N) of octets is observed. As the temperature is progressively lowered (b–d) $A_\beta{}^F$ becomes smaller (*cf.* Table III). Each octet progressively clarifies itself as a septet of doublets as the temperature is lowered.

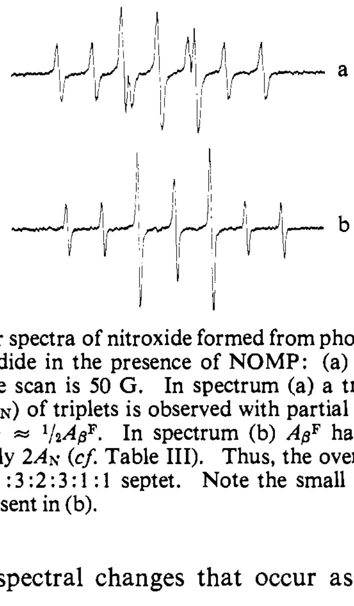


Figure 3. Esr spectra of nitroxide formed from photolysis of pentafluoroethyl iodide in the presence of NOMP: (a) 40°, (b) −60°. Each complete scan is 50 G. In spectrum (a) a triplet (equal intensities for A_N) of triplets is observed with partial fortuitous overlap due to $A_N \approx {}^1/_2A_\beta{}^F$. In spectrum (b) $A_\beta{}^F$ has increased to a value of exactly $2A_N$ (*cf.* Table III). Thus, the overlap is complete to form a 1:1:3:2:3:1:1 septet. Note the small $A_\gamma{}^F$ splitting in (a) which is absent in (b).

Discussion

Photolytic Stabilities of Fluoroalkyl Iodides. The causes of photolytic stability or instability of halogenated alkanes are difficult to define quantitatively. However, it is clear that the photolytic decompositions are more facile if the intermediate species formed are more stable. A lower energy barrier is required. For example, the higher quantum yield of $(CF_3)_2CF$ *vs.* CF_3 in solution must surely be a function of the stability of the two alkyl radicals involved.[19–21] (The fact that the

---

(19) It has been shown that in polyhalogenated alkanes the weakest carbon–halogen bond is ruptured most easily.[20]

(20) J. P. Simons and A. J. Yarwood, *Trans. Faraday Soc.*, 57, 2167 (1961); J. R. Majer and J. P. Simons, *Advan. Photochem.*, 2, 137 (1964).

(21) It has been reported that by far the most important process of

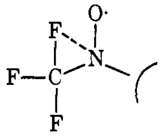
Table III.[a] Esr Temperature Study of Nitroxides Formed by the Photolysis of Fluoroalkyl Iodides in Methylene Chloride in the Presence of NOMP

Fluoroalkyl iodide	Temp, °C	A_N	$A_\beta{}^F$	$A_\gamma{}^F$
CF_3I	40	12.27	12.27	
	25	12.03	12.03	
	−30	11.99	12.14	
	−60	12.03	12.34	
	−90	11.81	12.38	
CF_3CF_2I	40	11.33	20.80	0.39
	25	11.25	21.16	0.43
	−30	11.28	22.27	0.34
	−60	11.31	22.65	0.22
	−90	11.32	23.15	<0.20
$CF_3CF_2CF_2I$	40	11.35	17.83	0.39
	25	11.34	17.64	0.39
	−30	11.44	17.80	0.68
	−60	11.29	17.56	0.71
	−90	11.39	17.49	0.76
$(CF_3)_2CFI$	40	12.10	2.30	2.30
	25	12.11	2.27	2.27
	−30	12.13	1.59	2.33
	−60	12.15	1.32	2.29
	−90	12.14	0.76	2.31

[a] These values were calculated in gauss from Fieldial calibrations. Each number is an average of several determinations. The reproducibility was usually within ±0.05 G and always within ±0.1 G. These deviations indicate that *small* trends with change in temperature should be accepted with caution.

photolyses are carried out in solution ensures that any excess energy due to the absorption of a photon will be lost extremely fast.) The data in Table II support the concept that thermodynamic stability of the intermediate fluoroalkyl radicals is proportional to the photolytic stability of the corresponding fluoroalkyl iodides. Thus, it is well known that the ability of a substituent to stabilize a free radical is in the order $C_6H_5 > Cl > F > H$. Table II illustrates that the photolytic stability is in the opposite order. The more stable the intermediate radical, the more easily the fluoroalkyl iodide decomposes upon photolysis.[22] As is obvious in Table II, two different series of competition photolyses were carried out. One is a series of R_fI *vs.* $CF_3CF_2CF_2I$ and the other is *vs.* $(CF_3)_2CFI$. The two different series were necessary due to experimental difficulties in the spectra analyses. In each case the analysis could only be made if a straight chain moiety was compared to an isopropyl moiety. However, the two series can be incorporated into one insofar as a qualitative order of radical stability is concerned. For example, experiment 3 in Table II shows the stability of $(CF_3)_3\dot{C}F > CF_3CF_2\dot{C}F_2$. Also, experiment 4 shows $CF_3CF_2\dot{C}F_2 > (CF_3)_2\dot{C}H$. Therefore, $(CF_3)_2\dot{C}F$ must be more stable than $(CF_3)_2\dot{C}H$. In addition, the percent values obtained for experiments 5 and 6 *vs.* 3 show that $(CF_3)_2\dot{C}C_6H_5 > (CF_3)_2\dot{C}Cl > (CF_3)_2\dot{C}F$. Then, overall, the preceding discussion and the data in Table II indicate radical stabilization ability for the following groups in the order $(CF_3)_2CC_6H_5 > (CF_3)_2CCl > (CF_3)_2CF > CF_3CF_2CF_2 > (CF_3)_2CH > CF_3CF_2 > CF_3$. Therefore, the following deductions can be made for specific groups in radical stabilization: $C_6H_5 > Cl > F > H$; and $CF_3CF_2 > CF_3 > F$. It appears that replacement of F by CF_3 (experiments 1 and 2) stabilizes a radical by slightly less than the replacement of F by Cl (experiments 3 and 5). Therefore, the best order is $C_6H_5 > Cl > CF_3 > F > H$. Consideration of experiments 1 and 3 (replacement of F by CF_3CF_2) yields the probable best overall order as $C_6H_5 > Cl \gtrsim CF_3CF_2 > CF_3 > F > H$. Apparently, perfluoroalkyl groups are able to spread the unpaired electron density over a larger area and, thus, are able to stabilize the free radicals to a greater extent than fluorine or hydrogen alone. This interpretation is in accord with the results of Park and coworkers,[24] who studied photochemical and free radical catalyzed additions of CF_3I and $CF_3CF_2CF_2I$ to ethylene and propargyl alcohol. The propyl iodide was found to be more efficient in these additions. A similar work by Brace[25] yielded additional insight. This worker found free radical catalyzed additions to olefins in the order $(CF_3)_2CFI > CF_3CF_2CF_2I > CF_3I$. Brace attributed this reactivity order to smaller dissociation energies of the higher iodides due to steric strain and resonance stabilization. Mentioned also was the possibility of greater polar resonance stabilization of the intermediate olefin–radical adducts; the higher perfluoro radical homologs would be most effective. This type of stabilization should not be important in the present work, however.

Temperature Study of Nitroxides. Esr analysis of the trifluoromethyl nitroxide derivative indicated a slight decrease in A_N and possibly a slight increase in A_F with temperature decrease (Table III). These results are in agreement with the work of Sheidler and Bolton[14] with the bistrifluoromethyl nitroxide. These workers reasoned that at lower temperature more effective fluorine–nitrogen p–π interactions would be possible, since better "bond" formation could occur with slower rotation. This bond formation is described as "partial conjugation of the fluorine p orbital with the nitrogen $2p_z$ orbital. This mechanism would result in a partial double bonding between the nitrogen and the CF_3 groups leading to partially hindered rotation about the C–N bonds." Transfer of spin would be to the fluorine atoms. It was noted that this interaction is a direct one with the π system in the sense of Sheppard's p–π interactions (*cf.* structure V). It is not a fluoride ion hyperconjugation mechanism. This explanation seems reasonable as an interpretation of the results in this paper for the trifluoromethyl nitroxide derivative.



V

Interpretation of the esr temperature study of the *t*-butylpentafluoroethyl nitroxide requires additional rationale. The exceedingly large increase in $A_\beta{}^F$ with temperature decrease while A_N remains constant cannot

---

photolysis of heptafluoro-*n*-propyl iodide is the carbon–iodine homolytic bond cleavage: D. A. Barr, W. C. Francis, and R. N. Haszedine, *Nature*, 177, 785 (1956).

(22) It should be added that the observed photolytic stability order is not predicted by consideration of a carbon–iodine bond weakening due to strong electron-withdrawing substituents (ability to stabilize anionic charge which is in the order $R_f > Cl > C_6H_5 > F > H$).[23]

(23) K. J. Klabunde, Ph.D. Thesis, University of Iowa, 1969.

(24) J. D. Park, F. E. Rogers, and J. R. Lacher, *J. Org. Chem.*, 26, 2089 (1961).

(25) N. O. Brace, *ibid.*, 28, 3093 (1963).

be due solely to fluorine–nitrogen p–π interactions (*cf.* Figure 3 and Table III). Piette, Ludwig, and Adams[26] have examined the esr spectra of several nitroaliphatic anion radicals and have found a dependence of A_{β}^{H} on spacial position with respect to the paramagnetic oxygen–nitrogen system. Conformational preferences were notable in the anion radicals when large alkyl groups were present. An angular dependence of A_{β}^{H} was found, and determined to be a function of the $\cos^2 \phi$. In addition, Gerlock and Janzen[27] have found angular dependence of A_{β}^{F} in their studies of perfluoroketyls, and have shown similarities in the angle dependencies for β-H and β-F atoms. Geske has extensively reviewed this area.[28]

The bulkiness of the fluorinated nitroxides examined in this paper suggests that conformational preferences at low temperature may be important. Indeed, examination of a model of the *t*-butylpentafluoroethyl nitroxide clearly indicates the preference of a conformer of minimum steric interactions. In this conformer ϕ is *ca.* 35°. (In this case ϕ is the angle between the β-fluorine, and the plane along the line of the carbon–nitrogen bond and perpendicular to the α-carbon–nitrogen–oxygen plane. With this conformation the trifluoromethyl group assumes a position in the proximity of the oxygen atom.) If the pentafluoroethyl group were freely and rapidly rotating about the carbon–nitrogen bond (rapidly with respect to the esr time scale), ϕ would be forced to assume an averaged value of 45°, or half of the two extremes of 90 and 0°. Thus, ϕ would be larger than 35° and A_{β}^{F} would be predicted as being smaller in the "averaged" conformer as in the preferred conformer by the $\cos^2 \phi$ function. At higher and higher temperatures, ϕ should approach the averaged value since rotation should occur faster with respect to the esr time scale. This rationale predicts that A_{β}^{F} should decrease with temperature increase. This trend is clearly indicated in Table III. Further studies discussed below also lend support to this idea.

A model of the *t*-butylheptafluoro-*n*-propyl nitroxide does not so easily reveal conformational preferences as in the pentafluoroethyl case considered previously. The data in Table III seem to indicate this fact since the changes in A_{β}^{F} and A_{γ}^{F} are relatively small. However, once again A_N does not change with temperature. If fluorine–nitrogen p–π interactions were the dominating factor, A_N should also change with temperature.[14] Therefore, the small variations in A_{β}^{F} and A_{γ}^{F} in this case are probably due to slight changes in the $\cos^2 \phi$ function and not p–π interactions.

The most convincing evidence for the $\cos^2 \phi$ argument in the determination of fluorine splitting constants in these systems was found upon esr analysis of the *t*-butylheptafluoroisopropyl nitroxide derivative. The scale model of this molecule clearly indicates a distinct conformational preference. The preferred conformer forces the β-fluorine atom into the same plane as the α-carbon–nitrogen–oxygen plane (ϕ 90°). This fluorine must also point directly away from and in opposite direction as the oxygen atom. Thus, as the time averaged value of ϕ approaches 90° (low temperature) A_{β}^{F} should become small as predicted by the $\cos^2 \phi$ function. Conversely, as the time averaged value of ϕ approaches 45° (high temperature) A_{β}^{F} should become larger. The predicted trend is clear in Table III. Note that all other splittings in this system remain essentially constant. Figure 2 illustrates the remarkable spectral changes with temperature.

Thus, fluorine nuclei esr splittings in these nitroxides are substantially affected by their spacial position with respect to the paramagnetic nitrogen–oxygen system. This positional dependence is a more reasonable interpretation of the data obtained from the temperature studies shown in Table III than the through space fluorine–nitrogen p–π interaction rationale.

Experimental Section

Trifluoromethyl iodide, pentafluoroethyl iodide, heptafluoro-*n*-propyl iodide, and heptafluoroisopropyl iodide were purchased from the Pierce Chem. Co. The gases were used directly and the liquids were stored over mercury metal in a refrigerator and filtered prior to use.

2-Hydro-2-iodohexfluoropropane. The preparation was carried out by the general method of Knunyants.[29,30] The crude product was purified by preparative phase glpc: bp 54°; $n^{20}\text{D}$ 1.3528; ^{1}H nmr δ 4.66 (septet, 1 H), J_{CF_3H} = 7.00 cps, ^{19}F nmr 65.67 ppm upfield from $CFCl_3$ (doublet, 6 F) (lit.[29] for 2-hydro-2-iodohexafluoropropane, bp 58°, $n^{20}\text{D}$ 1.3520).

2-Deuterio-2-iodohexafluoropropane. A 100-ml flask was charged with 3.57 g (0.108 mole) of methanol-O-*d*,[31] 8.45 g (0.108 mole) of dry dimethyl sulfoxide, 180 μl of triethylamine, and 3.0 g (0.0108 mole) of 2-hydro-2-iodohexafluoropropane. The flask was stoppered and stirred for 2 hr. The solution was syringed into a dilute aqueous hydrochloric acid solution and the bottom organic layer removed (*ca.* 2 g). The procedure was repeated with the recovered substrate. The final recovered material was purified by preparative glpc (0.5 g, 17%). Analysis by ^{19}F nmr indicated the product was 98–99% deuterated:[23] ^{19}F nmr 65.74 ppm upfield from $CFCl_3$ (singlet, 6 F).

2-Iodo-2-phenylhexafluoropropane. A 100-ml flask was charged with 7.6 g (0.050 mole) of anhydrous cesium fluoride, 7.6 g (0.030 mole) of iodine, 5.5 g (0.024 mole) of 2-phenylpentafluoropropene,[32] and 40 ml of dry N,N-dimethylformamide. The solution was stirred at 50° for 6 hr under a head of dry nitrogen. The mixture was poured over water, and the lower organic layer washed with a sodium bisulfite solution, water, dried, and distilled under vacuum to yield 3.0 g (35%) of 2-iodo-2-phenylhexafluoropropane: bp 49° (1 mm); ^{1}H nmr δ 7.83 (broad multiplet, 2 H), 7.15 (multiplet, 3 H); ^{19}F nmr 64.00 ppm upfield from $CFCl_3$ (singlet, 6 F). *Anal.* Calcd: C, 30.51; N, 1.41. Found: C 30.70; H, 1.41.

2-Chloro-2-iodohexafluoropropane. The preparation was carried out by the method of Mochalina and Dyatkin[33] by the decomposition of bistrifluoromethyldiazomethane[34] with iodine monochloride. The material was purified by preparative glpc (10% isolated yield).

Preparation of Esr Samples. All samples were prepared in a glass cell that was carefully kept covered with foil at all times (except for the photolysis period). The samples were photolyzed between 15 and 60 sec in a Rayonet photochemical reactor with 3500 Å light sources. The esr analyses were carried out on a Varian 4502 epr spectrometer.

A clean, dry esr cell was wrapped in foil and charged with 0.0018 g (2.1×10^{-5} mole) of NOMP. The cell was sealed by means of a rubber septum cap and 0.40 ml of solvent (benzene or methylene

---

(26) L. H. Piette, P. Ludwig, and R. N. Adams, *J. Am. Chem. Soc.*, **84**, 4212 (1962).

(27) J. L. Gerlock and E. G. Janzen, *J. Phys. Chem.*, 72, 1832 (1968); E. G. Janzen and J. L. Gerlock, *ibid.*, 71, 4577 (1967).

(28) D. H. Geske, *Progr. Phys. Org. Chem.*, **4**, 125, 179 (1967).

(29) B. L. Dyatkin, E. P. Mochalina, L. T. Lantseva, and I. L. Knunyants, *Chem. Abstr.*, 63, 14691*a* (1965).

(30) The author would like to thank Dr. C. G. Krespan and Dr. D. C. England of Dupont Chem. Co. for a generous supply of 2-hydrohexafluoroisobutyric acid.

(31) A. Streitweiser, Jr., L. Verbit, and P. Stang, *J. Org. Chem.*, **29**, 3706 (1964).

(32) F. E. Herkes and D. J. Burton, *J. Org. Chem.*, **32**, 1311 (1967).

(33) E. P. Mochalina and B. L. Dyatkin, *Bull. Acad. Sci. USSR*, **15**, 899 (1965).

(34) D. M. Gale, W. J. Middleton, and C. G. Krespan, *J. Am. Chem. Soc.*, 88, 3617 (1966).

chloride) syringed in. Then the fluoroalkyl iodide was syringed into the cell (usually *ca.* 4 μl, 0.0056 g, 2.5×10^{-5} mole). In the case of gases the substrate was distilled under vacuum into the esr cell by means of a small vacuum manifold. The solution was shaken vigorously and freeze degassed at least twice, warmed, photolyzed, and analyzed by esr.[35, 36]

Acknowledgment. The author is indebted to Dr. Donald J. Burton for helpful discussions, and to Phillips Petroleum Co. for financial aid.

---

(35) Freshly prepared solutions of NOMP had to be used for each sample, and remained diamagnetic if kept carefully covered from light. However, "aged" NOMP solutions became paramagnetic due to photolysis by visible light to form *t*-butyl radicals. NOMP is monomeric in solution and susceptible to photolysis, while it is a stable dimer in the solid state.[1]

(36) No esr signals were observed if the samples were not photolyzed.

Properties of Ion Pairs in Solution. The Reaction of Pyridinium Iodide Charge-Transfer Complexes with Methyl *p*-Toluenesulfonate

Raymond A. Mackay and Edward J. Poziomek

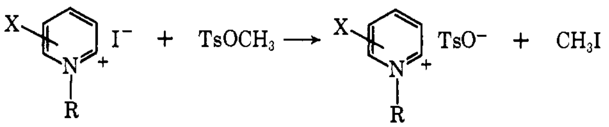
Contribution from the Physical Research Laboratory,
Edgewood Arsenal, Maryland 21010. *Received March 27, 1969*

Abstract: This paper presents a general survey of the relationships between some macroscopic and microscopic properties of pyridinium iodide salts in a variety of solvents. The properties investigated are transition energy (E_t), solubility (S), ion-pair dissociation constant (K_d), and rate constant for the nucleophilic displacement reaction of pyridinium iodide ion pairs (k_p) and free iodide ions (k_f) with methyl tosylate. In the absence of specific solvent–solute interactions, ion pair and neutral polar species are shown to exhibit similar solvation properties. The E_t values may be related to the kinetic and bulk thermodynamic parameters. Deviations which occur are related to specific interactions. The pyridinium iodide system is demonstrated to be of potentially great utility in the study of the solution properties of nonspherical cation–spherical anion ion pairs, the charge-transfer contribution to the ground state being small except at low E_t values.

A number of studies have been directed toward an examination of the effect of ion pairing on nucleophilic reactions, such as nucleophilic displacements by halide ions[1–3] and the alkylation of oxime salts.[4] A major difficulty in studies of this type is the lack of a method of directly following the ion pair concentration, since the ion pairs do not usually possess a readily measurable property (*e.g.*, a characteristic absorption band). The usual method employed in these kinetic studies is some form of titration which yields the total nucleophile concentration (*i.e.*, free ion plus ion pair). Conductance measurements may be used to obtain ion pair dissociation constants (K_d) which can then be applied to the kinetic data to obtain the rate constants k_f (for the free ion) and k_p (for the ion pair). However, care must be taken that any relationships obtained in this manner are not significantly sensitive to the value chosen for the distance parameter in the calculation of K_d.[3] A further consideration is that during a given kinetic run, the degree of dissociation (α) of the ion pair changes (except for isotopic exchange reactions). Therefore, in obtaining the apparent rate constant (k), initial rates (which are often difficult to obtain) should be used. The rate constant may be obtained by following the reaction over a period of time providing that the extent of reaction is large enough to give a sufficiently accurate value of k but small enough so that α does not change appreciably.[2, 3]

The pyridinium iodide ion pair has a characteristic charge transfer (c-t) absorption band in the visible or near uv, the frequency depending upon the substituent(s). The position of this c-t band for 4-carbomethoxy-1-ethylpyridinium iodide is the basis of Z values, an empirical measure of solvent polarity.[5] Thus, the concentration of the ion pair may be followed spectrophotometrically during the course of a reaction.

We have therefore decided to examine a nucleophilic displacement reaction involving pyridinium iodide. Methyl tosylate ($TsOCH_3$) undergoes an anion exchange reaction with 1-alkylpyridinium iodides in various solvents as shown in eq 1.[6,7] In the present paper we report the results of studies on this system.



(1)

Results

The salt used for the kinetic, dissociation, and solubility studies is 1-ethyl-4-cyanopyridinium iodide. This choice was based on its fairly good solubility in

---

(1) S. Winstein, L. G. Savedoff, S. Smith, I. D. R. Stevens, and J. S. Gall, *Tetrahedron Lett.*, 24 (1960).

(2) W. M. Weaver and J. D. Hutchison, *J. Amer. Chem. Soc.*, 86, 261 (1964).

(3) N. N. Lichtin, M. S. Puar, and B. Wasserman, *ibid.*, 89, 6677 (1967).

(4) S. G. Smith and D. V. Milligan, *ibid.*, 90, 2393 (1968).

(5) E. M. Kosower, *ibid.*, 80, 3253 (1958).

(6) E. J. Poziomek, unpublished results.

(7) This type of anion exchange reaction with 1-alkylpyridinium iodides has been used for synthetic purposes. For example, see B. E. Hackley, Jr., E. J. Poziomek, G. M. Steinberg, and W. A. Mosher, *J. Org. Chem.*, 27, 4220 (1962).